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FORM PTO-1390 U.S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		50395-109
		U.S. APPLIC. NO. (if known, see 37 CFR 1.5) 10/030312
INTERNATIONAL APPLICATION NO. PCT/JP00/04719	INTERNATIONAL FILING DATE July 13, 2000	PRIORITY DATE CLAIMED July 19, 1999

TITLE OF INVENTION

SEPARATOR FOR SOLID POLYMER ELECTROLYTIC FUEL BATTERY

APPLICANTS FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendment has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information
    1. International Search Report
    2. First Page of Published Application.

20277

PATENT TRADEMARK OFFICE

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U.S. APPLIC. NO. (if known, see 37 CFR 1.50)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/030312	PCT/JP00/04719	50395-109

				CALCULATIONS	PTO USE ONLY
17. ☒ The following fees are submitted: **Basic National Fee (37 CFR 1.492(a)(1)-(5)):** Search Report has been prepared by the EPO or JPO $890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) $710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) $740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO $1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				$ 0.00	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				$ 0.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	9 -20 =	0	x $18.00	$0.00	
Independent Claims	1 -3 =	0	x $84.00	$ 0.00	
Multiple dependent claim(s) (if applicable)			+ $280.00	$ 0.00	
TOTAL OF ABOVE CALCULATIONS =				$0.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ 0.00	
SUBTOTAL =				$ 890.00	
Processing fee of $130.00 for furnishing the English translation later than the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0.00	
TOTAL NATIONAL FEE =				$ 890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$ 40.00	
TOTAL FEES ENCLOSED =				$930.00	
				Amount to be: refunded	$
				charged	$ 930.00

a. ☐ A check in the amount of $ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 500417 in the amount of $ 930.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 500417. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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26,106
REGISTRATION NUMBER

January 10, 2002
DATE

Docket No.: 50395-109

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :
Nobuyuki OKUDA, et al. :
Serial No.: : Group Art Unit:
Filed: January 10, 2002 : Examiner:

For: SEPARATOR FOR SOLID POLYMER ELECTROLYTIC FUEL BATTERY

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, DC 20231

Sir:

Prior to examination of the above-referenced application, please amend the application as follows:

IN THE CLAIMS:

Please amend the claims 4-9 as follows:

4. (Amended) A separator for a solid polymer electrolyte type fuel claimed in claim 1, wherein the micro-Vickers hardness or the Knoop hardness of the conducting hard carbon film is a hardness of not less than 8GPa.

5. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in claim 1, wherein the resistivity of the conducting hard carbon film is $5x10^{-4}$ to 10 Ωcm.

6. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in claim 1, wherein the hydrogen content of the conducting hard carbon film is less than 1 atom%

7. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in claim 1, wherein at least one element among the elements constituting the separator substrate or the intermediate layer is included in the conducting hard carbon film.

8. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in claim 1, wherein the conducting hard carbon film is formed by sputtering or cathode ark ion plating using solid carbon as the process material or by plasma CVD or ionized vapor deposition using a hydrocarbon gas as the process material.

9. (Amended) A solid polymer electrolyte type fuel cell using a separator claimed in claim 1.

REMARKS

The above-referenced application is amended to delete the multiple dependency of claims 4-9 to avoid the multiple dependent claims filing fee. Attached hereto is a marked-up version of the changes made to claims 4-9. Entry of this Preliminary Amendment is respectfully requested.

Respectfully submitted,

MCDERMOTT, WILL & EMERY

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MARKED-UP VERSION OF CLAIMS 4-9

IN THE CLAIMS:

Please amend the claims 4-9 as follows:

4. (Amended) A separator for a solid polymer electrolyte type fuel claimed in [any one of] claim[s] 1 [through 3], wherein the micro-Vickers hardness or the Knoop hardness of the conducting hard carbon film is a hardness of not less than 8GPa.

5. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in [any one of] claim[s] 1 [through 4], wherein the resistivity of the conducting hard carbon film is $5x10^{-4}$ to 10 Ωcm.

6. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in [any one of] claim[s] 1 [through 5], wherein the hydrogen content of the conducting hard carbon film is less than 1 atom%

7. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in [any one of] claim[s] 1 [through 6] 1, wherein at least one element among the elements constituting the separator substrate or the intermediate layer is included in the conducting hard carbon film.

8. (Amended) A separator for a solid polymer electrolyte type fuel cell claimed in [any one of] claim[s] 1 [through 7], wherein the conducting hard carbon film is formed by sputtering or cathode ark ion plating using solid carbon as the process material or by plasma CVD or ionized vapor deposition using a hydrocarbon gas as the process material.

9. (Amended) A solid polymer electrolyte type fuel cell using a separator claimed in [any one of] claim[s] 1 [through 8].

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DESCRIPTION

SEPARATOR FOR SOLID POLYMER ELECTROLYTIC FUEL BATTERY

Technical Field

This invention relates to a separator for a fuel cell capable of lowering the internal resistance of the fuel cell, and to a solid polymer electrolyte type fuel cell using this separator.

Background Art

Figure 1 shows a schematic view of a single solid polymer electrolyte fuel cell. This single cell consists of a solid polymer electrolyte film 1; catalyst electrode layers 2, 3 disposed on either side of the solid polymer electrolyte film 1; gas diffusion electrodes 4, 5 disposed on the outer sides of the catalyst electrode layers 2, 3; and separators 6, 7 disposed on the outer sides of the gas diffusion electrodes 4, 5.

In a cell of this kind, when a fuel gas (for example hydrogen) is passed through the gas diffusion electrode 4 and an oxidizing gas (for example oxygen gas) is passed through the gas diffusion electrode 5, an electrochemical reaction occurs through the solid polymer electrolyte, and electrons are produced. By these electrons being extracted to an external circuit by the path from the catalyst electrode layers to the gas diffusion electrodes and from the gas diffusion electrodes to the separators, electrical energy is produced.

A single cell can produce about 1 volt, and in practice multiple cells are stacked to make a fuel cell stack.

The operating principle of this kind of fuel cell is such that the separator surfaces must have good electrical conductivity. And because they are exposed to fuel gas or oxidizing gas, the separators must also be made of a material having a high resistance to corrosion. Because of this, the use of carbon materials for separators has been studied (TOYOTA Technical Review Vol. 47, No. 2, Nov. 1997 pp.70-75, and Japanese Unexamined Patent Publication No. H.7-272731). However, because carbon materials have low mechanical strength, there is the drawback of having to use a relatively thick separator and consequently the stack becomes long in length and thus large in size. And at the same time, when the fuel cell is mounted in an automobile or the like, breakage of the separators caused by vibration has been considered a problem.

In view of this, methods using metal plates have been studied; however, metals and alloys having the required corrosion resistance are often expensive. The disadvantage of relatively low cost stainless steel and aluminum alloys is their insufficient corrosion resistance, which causes an increase of the contact resistance and consequently the rise of internal resistance of the fuel cell.

With respect to this problem, for example in Japanese Unexamined Patent Publication No. H.10-308226, a solid polymer electrolyte fuel cell has been proposed wherein a separator substrate is made of aluminum, iron or stainless steel or the like and, a film including carbon is adhered to at least

the face of the surface thereof, to make contact with a gas diffusion electrode. There has also been proposed in Japanese Unexamined Patent Publication No. 2000-67881, a separator for a fuel cell made by covering a metal plate having a low electrical resistance with an amorphous carbon film whose hydrogen content is between 1 atom% and 20 atom%. However, because such carbon films and amorphous carbon films have low mechanical strength, that is, because their film hardness is low, the carbon films or amorphous carbon films have had problems with damage by vibration when mounted on a vehicle and the corrosion resistance is lost.

Disclosure of Invention

It is therefore an object of the present invention to provide a separator with superior corrosion resistance and a fuel cell with a minimal internal resistance.

To achieve this object and other objects, the present invention provides a separator for a solid polymer electrolyte type fuel cell, wherein multiple single cells are laminated and made up of a solid polymer electrolyte layer and catalyst electrode layers, gas diffusion electrodes and separators disposed on either side of the solid polymer electrolyte layer: wherein the separator has a separator substrate made of a metal or the like having a high mechanical strength, and at least a part of the surface of the separator substrate to make contact with a gas diffusion electrode is covered with an electrically conducting hard carbon film having excellent conductivity and corrosion

resistance and provides a solid polymer electrolyte type fuel cell using this separator.

Although in the invention the material and the shape of the separator substrate are not particularly limited, a material having a mechanical strength sufficient for its use in a fuel cell for an automotive vehicle is preferable, and also a shape forming a structure having a strength sufficient for its use in a fuel cell for an automotive vehicle is preferable. The conducting hard carbon film is formed either directly on the surface of the separator substrate or with an intermediate layer therebetween. The conducting hard carbon film has a hardness of not less than 8GPa by micro-Vickers hardness or Knoop hardness. The conducting hard carbon film has a resistivity of 5×10^{-4} to 10 Ωcm. The hydrogen content of the conducting hard carbon film is less than 1 atom%. And at least one element constituting the separator substrate or the intermediate layer is included in the conducting hard carbon film.

The intermediate layer is a single-layer film of one from among, or a laminate film or a mixture film including two or more from among, carbides, nitrides and carbo-nitrides of metals, and particularly carbides, nitrides and carbo-nitrides of metals which are elements of group IVa, Va or VIa of the periodic table.

The conducting hard carbon film is formed by sputtering or cathode ark ion plating using solid carbon as the process material, or by plasma CVD or ionized vapor deposition using a hydrocarbon gas as the process material.

According to the invention, because a freely chosen separator substrate is coated with a conducting hard carbon film having excellent corrosion resistance, a rise of the contact resistance at the separator surface due to corrosion is prevented. This is because the conducting hard carbon film itself has extremely good corrosion resistance and does not form a substance with a high electrical resistance, such as a passive film, on its surface.

As well as having excellent adhesion strength a hard carbon film has a high film hardness, and because cracking caused by vibrations in a vehicle or the like does not readily occur, it is possible to produce a highly reliable separator. The hardness of the hard carbon film is preferably not less then 8GPa by micro-Vickers hardness or Knoop hardness. By using a high-hardness film of this kind, it is possible to obtain durability with respect to vibrations in a vehicle and the like. For the hardness measurement, either the micro-Vickers hardness is measured using a Vickers indentor with a pressing load of 0.49N or less or the Knoop hardness is measured using a Knoop indenter with a pressing load of 0.49N or less.

For the hard carbon film, diamond-like carbon (DLC) is a typical material; however, it is known that ordinary DLC has a high electrical resistance and often exhibits insulativity. Such an insulating or high-resistance DLC is unsuitable for this application. A low-resistance DLC is desirable. The value of the electrical resistance is preferably in the range of 5×10^{-4} to 10 Ωcm. A hard carbon film of less than 5×10^{-4} Ωcm is undesirable because it will also have a low film hardness (lower than 8GPa by micro-

Vickers hardness). A value over 10 Ωcm is undesirable because the contact resistance will be high. In the resistance measuring method, the surface of an insulating substrate (for example silica glass) is coated with the subject film of the measurement. The measuring method called the four-terminal method is used.

The hydrogen content of this low-resistance hard carbon film is preferably less than 1 atom%. A hard carbon film with a hydrogen content of more than 1 atom% is undesirable because it will not have a low contact resistance. Also, by forming the hard carbon film so that an element of the separator substrate or the intermediate layer mixes with the film and thus at least one element constituting the separator substrate or the intermediate layer is included in the conducting hard carbon film, it is possible to form a good-quality conducting hard carbon film whose adherence is high and which does not readily flake off.

Particularly when a soft metal is used for the separator substrate, it is preferable for an intermediate layer made of a hard material to be interposed between the separator substrate and the hard carbon film. This hard intermediate layer is preferably a single-layer of one from among, or multiple layers or a mixture including two or more from among, carbides, nitrides and carbo-nitrides of the periodic table group IVa, Va and VIa metals. These intermediate layer materials all have a high micro-Vickers hardness of 10GPa or more and have the effect of raising the durability of the hard carbon film with respect to cracking.

A preferable method for coating the high-hardness, conducting hard carbon film is sputtering or cathode ark ion plating using solid carbon as the process material or plasma CVD or ionized vapor deposition using a hydrocarbon gas as the process material. By using one of these methods it is possible to obtain excellent adhesion strength at the same time.

Brief Description of the Drawings

Figure 1 is a schematic view of a single cell of a solid polymer electrolyte fuel cell; and

Figure 2 is a graph showing a distribution of Cr density in a sample pertaining to a fourth preferred embodiment of the invention.

Explanation of the Referenced Numbers

1 is a solid polymer electrolyte film; 2, 3 are catalyst electrode layers; 4, 5 are gas diffusion electrodes; 6, 7 are separators; 8 is a fuel gas; 9 is an oxidant gas; 10 is a voltage meter; 11 is load resistance (1 Ω); 12 is an ammeter.

Best Mode for Carrying out the Invention

Specific preferred embodiments of the invention will now be described; however, the invention is not limited to these preferred embodiments.

Embodiment 1

Surface coating layers having the film materials and film structures shown in Table I were coated using different methods on one side of a separator substrate made of SUS 304. In the table, ' ark' in the coating

method column is an abbreviation of cathode ark ion plating. For comparison, samples made by applying gold plating or lead-carbon compound plating to one side of a separator substrate made of SUS 304 were also prepared. A single cell was assembled by bringing into contact these separators, gas diffusion electrodes (porous graphite plates with polytetrafluoroethylene as a binder) and a solid polymer electrolyte (covered on a positive electrode side with a Pt catalyst and on a negative electrode side with a Pt-Ru catalyst) to form the structure shown in Fig. 1, and electricity was actually generated using hydrogen and oxygen.

The current density at the time of generation was made 0.1 A/cm^2. For the time variation of the resistance between the separators and the gas diffusion electrodes, before generation and after predetermined periods of generation the resistance between 2 and 6 in Fig. 1 was measured and tabled with the initial resistance made 1. And before the fuel cell was actually assembled, an operation of lightly rubbing the separators and the gas diffusion electrodes was carried out on all of the samples according to the invention and the comparison examples, to simulate damage to the surface coating layers caused by vibrations in a vehicle. The results are shown in Table I. It is clear from Table I that the samples according to the invention exhibit stable internal resistance in Protracted generating operation.

Table I

	Sample no.	intermediate layer			Conducting hard carbon film				Variation with time of internal resistance (initial value taken as 1)		
		material	thickness (μm)	method	thickness (μm)	method	hardness (GPa)	resistivity (Ω cm)	before start	after 5 hrs	after 100 hrs
Preferred embodiment	1	–	–	–	1.2	sputtering	10	3×10^{-3}	1.00	1.00	1.03
	2	–	–	–	0.5	ark	18	5×10^{-2}	1.00	1.02	1.05
	3	TiN	1.5	ark	0.2	sputtering	13	6×10^{-4}	1.00	1.01	1.07
	4	ZrCN	2.5	ark	0.3	ark	15	4	1.00	1.00	1.03
	5	HfC	3.5	sputtering	1.6	sputtering	9	5	1.00	1.00	1.02
	6	VN	0.8	ark	1.4	plasma CVD	30	3	1.00	1.00	1.05
	7	NbC	1.3	sputtering	1.5	sputtering	8.5	8×10^{-2}	1.00	1.00	1.02
	8	TaCN	2	ark	1.1	ionized vapor deposition	22	7	1.00	1.03	1.07
	9	CrN	1.5	ark	0.9	sputtering	17	2×10^{-2}	1.00	1.00	1.03
	10	MoC	3	sputtering	2.5	ark	16	4×10^{-1}	1.00	1.00	1.01
	11	WC	2	sputtering	2.4	plasma CVD	25	5×10^{-1}	1.00	1.00	1.02
	12	CrN	0.7	ionized vapor deposition	1.2	ionized vapor deposition	11	2×10^{-3}	1.00	1.00	1.01
	13	–	–	–	1.1	ark	12	7×10^{-2}	1.00	1.05	1.40
	14	–	–	–	1.3	plasma CVD	28	5	1.00	1.25	1.50
	15	CrCN	1.5	ark	1.2	sputtering	16	7×10^{-3}	1.00	1.02	1.06
	16	NbC	2.5	ark	1.1	ark	9	4	1.00	1.40	1.75
	17	WC	3.5	sputtering	1.3	plasma CVD	30	3	1.00	1.30	1.43
	18	CrN	0.5	ark	0.5	ark	20	5×10^{-1}	1.00	1.00	1.01
Comparison example	19	gold plating	5	wet plating	–	–	–	–	1.00	5.05	*
	20	Pb-C plating	10	dispersion plating	–	–	–	–	1.00	5.35	*
	21	– (substrate only)							1.00	9.86	*

* generation impossible due to rise of internal resistance

Embodiment 2

As in the first preferred embodiment, surface coating layers having the film materials and film structures shown in Table II were coated by using different methods onto one side of a separator substrate made of SUS 316. For comparison, samples made by applying gold plating or lead-carbon compound plating to one side of a separator substrate made of SUS 316 were also prepared. A single cell was assembled by bringing into contact these separators, gas diffusion electrodes (porous graphite plates with polytetrafluoroethylene as a binder) and a solid polymer electrolyte (covered on a positive electrode side with a Pt catalyst and on a negative electrode side with a Pt-Ru catalyst) to form the structure shown in Fig. 1, and electricity was generated using hydrogen and oxygen.

The current density at the time of generation was made 0.1 A/cm^2. The variation with time of the resistance between the separators and the gas diffusion electrodes was measured by the same method as in the first preferred embodiment. And before the fuel cell was actually assembled, an operation of lightly rubbing the separators and the gas diffusion electrodes was carried out on all of the samples according to the invention and the comparison examples, to simulate damage to the surface coating layers caused by vibrations in a vehicle. The results are shown in Table II. It is clear from Table II that the samples according to the invention exhibited stable internal resistance under prolonged generating operation.

Table II

	Sample no.	intermediate layer			Conducting hard carbon film				Variation with time of internal resistance (initial value taken as 1)		
		material	thickness (μm)	method	thickness (μm)	method	hardness (GPa)	resistivity (Ω cm)	before start	after 5 hrs	after 100 hrs
Preferred embodiment	22	–	–	–	1.2	sputtering	11	2×10^{-3}	1.00	1.00	1.01
	23	–	–	–	0.5	ark	18	5×10^{-2}	1.00	1.00	1.02
	24	TiN	1.5	ark	0.2	sputtering	13	6×10^{-4}	1.00	1.01	1.08
	25	ZrCN	2.5	ark	0.3	ark	17	7	1.00	1.00	1.01
	26	HfC	3.5	sputtering	1.6	sputtering	8	5	1.00	1.00	1.01
	27	VN	0.8	ark	1.4	plasma CVD	28	4	1.00	1.00	1.02
	28	NbC	1.3	sputtering	1.5	sputtering	8.5	9×10^{-2}	1.00	1.00	1.01
	29	TaCN	2	ark	1.1	ionized vapor deposition	22	6	1.00	1.01	1.05
	30	CrN	1.5	ark	0.9	sputtering	10	3×10^{-2}	1.00	1.00	1.02
	31	MoC	3	sputtering	2.5	ark	16	4×10^{-1}	1.00	1.00	1.01
	32	WC	2	sputtering	2.4	plasma CVD	25	5	1.00	1.00	1.01
	33	CrN	0.7	ionized vapor deposition	1.2	ionized vapor deposition	12	6×10^{-3}	1.00	1.00	1.02
	34	–	–	–	1.1	ark	11	5×10^{-2}	1.00	1.05	1.38
	35	–	–	–	1.3	plasma CVD	30	8	1.00	1.15	1.40
	36	CrCN	1.5	ark	1.2	sputtering	16	6×10^{-2}	1.00	1.02	1.07
	37	NbC	2.5	ark	1.1	ark	9	6	1.00	1.40	1.75
	38	WC	3.5	sputtering	1.3	plasma CVD	32	5	1.00	1.30	1.41
	39	CrN	0.5	ark	0.5	ark	19	7×10^{-1}	1.00	1.00	1.01
Comparison example	40	gold plating	5	wet plating	–	–	–	–	1.00	4.80	*
	41	Pb-C plating	10	dispersion plating	–	–	–	–	1.00	5.12	*
	42	– (substrate only)							1.00	8.50	*

* generation impossible due to rise of internal resistance

Embodiment 3

As in the first and second preferred embodiments, surface coating layers having the film materials and film structures shown in Table III were coated by using different methods onto one side of a separator substrate made of an aluminum alloy including 96 wt% aluminum, namely alloy number A5052 specified in JIS-H4000. For comparison, samples made by applying gold plating or lead-carbon compound plating to one side of a separator substrate made of the same aluminum alloy were also prepared. A single cell was assembled by bringing into contact these separators, gas diffusion electrodes (porous graphite plates with polytetrafluoroethylene as a binder) and a solid polymer electrolyte (covered on a positive electrode side with a Pt catalyst and on a negative electrode side with a Pt-Ru catalyst) to form the structure in Fig. 1, and electricity was generated using hydrogen and oxygen.

The current density at the time of generation was made 0.1 A/cm^2. The variation with time of the resistance between the separators and the gas diffusion electrodes was measured by the same method as in the first preferred embodiment. And before the fuel cell was actually assembled, an operation of lightly rubbing the separators and the gas diffusion electrodes was carried out on all of the samples according to the invention and the comparison examples, to simulate damage to the surface coating layers caused by vibrations in a vehicle. The results are shown in Table III. It is clear from Table III that the samples according to the invention exhibited

stable internal resistance in long period generating operation.

Table III

	Sample no.	intermediate layer			Conducting hard carbon film					Variation with time of internal resistance (initial value taken as 1)		
		material	thickness (μm)	method	thickness (μm)	method	hardness (GPa)	resistivity (Ω cm)	hydrogen content (atom %)	before start	after 5 hrs	after 100 hrs
Preferred embodiment	43	–	–	–	1.2	sputtering	15	4×10^{-3}	0.5	1.00	1.01	1.05
	44	–	–	–	0.5	ark	19	3×10^{-2}	0.3	1.00	1.05	1.20
	45	TiN	1.5	ark	0.2	sputtering	12	5×10^{-4}	0.6	1.00	1.01	1.08
	46	ZrCN	2.5	ark	0.3	ark	11	2	0.3	1.00	1.00	1.01
	47	HfC	3.5	sputtering	1.6	sputtering	7	7	0.8	1.00	1.00	1.01
	48	VN	0.8	ark	1.4	plasma CVD	21	6	5.0	1.00	1.00	1.02
	49	NbC	1.3	sputtering	1.5	sputtering	8.5	7×10^{-2}	0.4	1.00	1.00	1.01
	50	TaCN	2	ark	1.1	ionized vapor deposition	22	4	0.5	1.00	1.01	1.11
	51	CrN	1.5	ark	0.9	sputtering	12	8×10^{-3}	0.2	1.00	1.00	1.02
	52	MoC	3	sputtering	2.5	ark	16	5×10^{-1}	0.6	1.00	1.00	1.01
	53	WC	2	sputtering	2.4	plasma CVD	27	3	3.8	1.00	1.00	1.01
	54	CrN	0.7	ionized vapor deposition	1.2	ionized vapor deposition	16	20	0.9	1.00	1.00	1.02
	55	–	–	–	1.1	ark	9	12	0.7	1.00	1.03	1.09
	56	–	–	–	1.3	plasma CVD	31	8	0.9	1.00	1.01	1.03
	57	CrN	1.5	ark	1.2	sputtering	10	5×10^{-3}	0.5	1.00	1.02	1.05
	58	NbC	2.5	ark	1.1	ark	9	2	0.8	1.00	1.40	1.79
	59	WC	3.5	sputtering	1.3	plasma CVD	24	3	4.5	1.00	1.30	1.36
	60	CrN	0.5	ark	0.5	ark	22	2×10^{-1}	0.3	1.00	1.00	1.01
Comparison example	61	gold plating	5	wet plating	–	–	–	–	–	1.00	6.21	*
	62	Pb-C plating	10	dispersion plating	–	–	–	–	–	1.00	7.51	*
	63	– (substrate only)								1.00	12.30	*

* generation impossible due to rise of internal resistance

Embodiment 4

Surface coating layers having the film materials and film structures shown in Table IV were coated by cathode ark ion plating onto one side of a separator substrate made of SUS 304. In sample no. 64, first only the intermediate layer was deposited, then for one minute the intermediate layer and the conducting hard carbon film were deposited simultaneously, and then only the conducting hard carbon film was deposited. In sample no. 65, first only the intermediate layer was deposited and then only the conducting hard carbon film was deposited. When the respective variations of internal resistance with time were measured, it was found that in sample no. 64 the internal resistance had not risen substantially even after 200 hours, which is an excellent characteristic.

Table IV

Sample no.	Intermediate layer			Conducting hard carbon film						Variation with time of internal resistance (initial value taken as 1)		
	material	thickness (μm)	method	thickness (μm)	method	hardness (GPa)	resistivity (Ω cm)	duration of simultaneous deposition with intermediate layer	hydrogen content (atom %)	before start	after 5 hrs	after 200 hrs
64	CrN	about 1.0	ark	about 1.0	ark	23	5×10^{-1}	1 min.	0.6	1.00	1.00	1.01
65	CrN	1.0	ark	1.0	ark	23	5×10^{-1}	none	0.4	1.00	1.00	1.05

When the Cr density in the depth direction of the film was analyzed with a Secondary Ion Mass Spectrometer (SIMS), it was found that in sample no. 64, Cr was included in the conducting carbon film as shown in Fig. 2. In sample no. 65, on the other hand, almost no Cr was included in the conducting carbon film.

Industrial Applicability

With this invention it is possible to obtain a solid polymer electrolyte type fuel cell having high reliability over a long period.

CLAIMS:

1. A separator for a solid polymer electrolyte type fuel cell wherein multipile single cells are laminated and made up of a solid polymer electrolyte layer and catalyst electrode layers, gas diffusion electrodes and separators disposed on either side of the solid polymer electrolyte layer, wherein at least a part thereof to make contact with a gas diffusion electrode is covered with an electrically conducting hard carbon film.

2. A separator for a solid polymer electrolyte type fuel cell claimed in claim 1, wherein an intermediate layer comprising a single layer film of one compound from among the group consisting of metal carbides, metal nitrides and metal carbo-nitrides or a laminate film or a mixture film including two or more compounds from among the same group is interposed between the conducting hard carbon film and the separator substrate.

3. A separator for a solid polymer electrolyte type fuel cell claimed in claim 2, wherein a metal of the metal carbide, metal nitride or metal carbo-nitride of the intermediate layer is an element or two or more elements of group IVa, Va or VIa.

4. A separator for a solid polymer electrolyte type fuel cell claimed in any one of claims 1 through 3, wherein the micro-Vickers hardness or the Knoop hardness of the conducting hard carbon film is a hardness of not less than 8GPa.

5. A separator for a solid polymer electrolyte type fuel cell claimed in any one of claims 1 through 4, wherein the resistivity of the conducting

hard carbon film is 5×10^{-4} to 10 Ωcm.

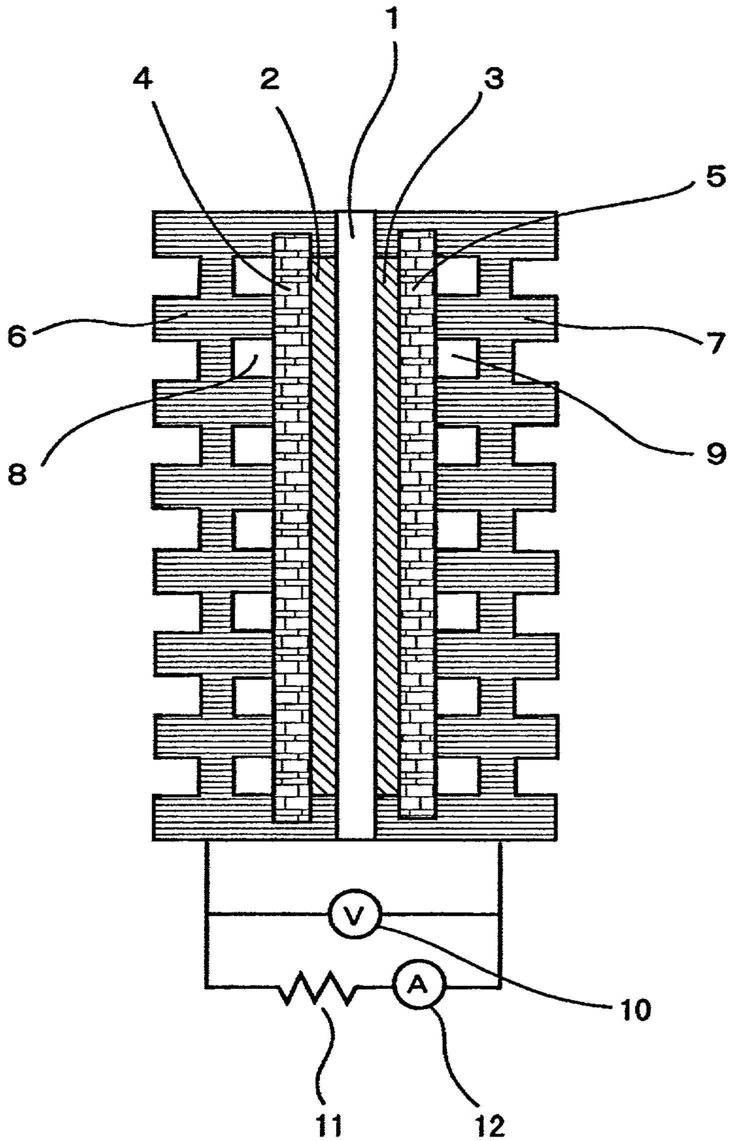
6. A separator for a solid polymer electrolyte type fuel cell claimed in any one of claims 1 through 5, wherein the hydrogen content of the conducting hard carbon film is less than 1 atom%.

7. A separator for a solid polymer electrolyte type fuel cell claimed in any one of claims 1 through 6, wherein at least one element among the elements constituting the separator substrate or the intermediate layer is included in the conducting hard carbon film.

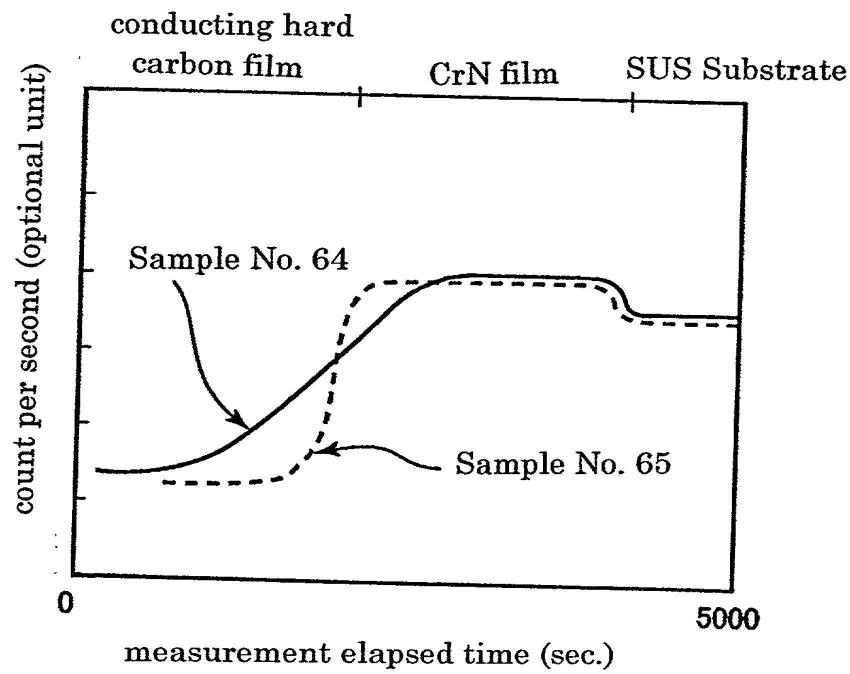
8. A separator for a solid polymer electrolyte type fuel cell claimed in any one of claims 1 through 7, wherein the conducting hard carbon film is formed by sputtering or cathode ark ion plating using solid carbon as the process material or by plasma CVD or ionized vapor deposition using a hydrocarbon gas as the process material.

9. A solid polymer electrolyte type fuel cell using a separator claimed in any one of claims 1 through 8.

F I G. 1



F I G. 2


conducting hard carbon film
CrN film
SUS Substrate
count per second (optional unit)
Sample No. 64
Sample No. 65
0
5000
measurement elapsed time (sec.)

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Application(s)	Attorney's Docket Number

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SEPARATOR FOR SOLID POLYMER ELECTROLYTIC FUEL BATTERY

the specification of which:

☐ is attached hereto.

☐ was filed as United States application Serial No. ______

on ______

and was amended on ______ (if applicable).

☒ was filed as PCT international application Number ***PCT/JP00/04719***

on ***July 13, 2000***

and was amended under PCT Article 19 on ______ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is known to me to be material to patentability in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or Section 365(b) of any foreign and/or international application(s) for patent or inventor's certificate or Section 365(a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (If PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Japan	***204173/1999***	***19 / July / 1999***	☒Yes ☐ No

I hereby claim the benefit under 35 USC §119(e) of any United States provisional application(s) listed below.

PRIOR PROVISIONAL APPLICATION(S):

Application Number	Filing Date

100124-US-00 2/4

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s), or §365(c) of any PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS			STATUS (Check One)		
U.S. Application Number	U.S. Filing Date		Patented	Pending	Abandoned
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT Application No.	PCT Filing Date	U.S. Serial Numbers Assigned *(if any)*			

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100124-US 00 3/4

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I hereby declare that all statement made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Date Jan. 11. 2001	Date JUN. 11. 2001	Date Jun. 11. 2001

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